III.B.10 Modification of Nickel-YSZ Anodes for Control of Activity and Stability from Carbon Formation during SOFC Operation

Objectives

- Quantify methane steam reforming activity of Ni-yttria-stabilized zirconia (YSZ) anode as a function of processing and operating conditions and pre-treatment.
- Develop methods to adjust and control Ni-YSZ anode activity to provide good thermal management and efficiency for methane on-anode reforming.
- Determine the activity and thermal profile of Ni-YSZ anode wafers under steam methane reforming and compare results with previous powder test results and computational modeling calculations.
- Measure effect of anode formulation on susceptibility toward carbon formation as a function of S/C ratio and concentration of higher hydrocarbons in natural gas.

Accomplishments

- Measured kinetic activity of Ni-YSZ anodes.
- Utilized transmission electron microscopy (TEM) methods to display the formation and sintering of small Ni crystallites present in Ni-YSZ anodes following reduction and steam reforming.
- Designed and constructed new reactor system for anode wafer testing for methane steam reforming.
- Validated thermogravimetric analysis (TGA) method as a viable approach for quantifying and comparing catalysts for carbon formation as function of catalyst composition and reaction conditions.
- Demonstrated the tolerance to carbon formation at low S/C ratios through MgO addition to Ni-YSZ anodes.

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Introduction

During FY 2006, the SECA Core Technology program in Fuel Reforming at Pacific Northwest National Laboratory (PNNL) continued its work on Ni/YSZ anodes and the topic of on-anode reforming of methane and natural gas. A major focus was to quantify anode activity and activity maintenance and to bring this in balance with electrochemical (H_2 and CO oxidation) activity. A second focus was to quantify the potential of MgO addition to Ni-YSZ to reduce the propensity of carbon formation, allowing operation at low S/C ratios. Both efforts are aimed at promoting the thermal efficiency of operation of the fuel cell.

One area of concern is the fact that our Ni-YSZ samples showed significant deactivation during methane steam reforming powder tests at high space velocities. We have substantial evidence that this is a result of Ni sintering under reaction conditions. This sintering behavior must be understood and controlled in order to establish reproducible anode activity. With this in hand, we can proceed to determine if this activity is too high or too low relative to what is required for proper thermal management of the anode, and determine what steps need to be taken to bring this activity in line with requirements. This activity measurement needs to be supplemented with tests of formed anodes, in order to include effects of heat and mass transport on performance and to measure thermal profiles. This work is just initiating, and we describe progress in reactor design and construction. Because of the potential confusion between sintering and carbon-based catalyst deactivation, we have initiated studies using thermogravimetric methods to quantify carbon deposition as a function of operating parameters. Representative results are also reported.

Approach

Our approach has been to study the performance of anode formulations for methane steam reforming in the absence of electrochemical activity, in order to determine the "open circuit" contribution to overall performance as a result of surface structure and

composition. Ni-YSZ formulations have been tested as diluted powders in flow-through tests at high space velocities in order to obtain kinetic information. Because of significant activity declines observed with the freshly reduced Ni-YSZ anodes, we initiated a series of TEM, x-ray diffraction (XRD), and chemisorption studies to look for evidence of nickel metal sintering and/or carbon formation on a series of Ni-YSZ samples, including freshly sintered, following reduction, and following reaction. The next phase, just initiated, will look at testing formed pieces under flow-by operation and much lower space velocities. In the latter case, we will be measuring thermal profile along the flow axis of the Ni-YSZ plate. This will provide critical information on what treatments will be necessary to optimize the reforming activity to match the electrochemical activity and avoid thermal gradients.

To measure resistance to carbon formation, our approach has been a combination of TGA studies coupled with reactor testing. TGA analysis carried out under reaction conditions allows measurement of weight gain, which can be attributed to carbon formation. Reactor testing provides additional information on longer term performance.

Results

Ni-YSZ Activity and TEM Measurements

Our reforming tests with Ni-YSZ as powders have shown an initial decline in activity, lining out at some final value after several hours on-stream. Figure 1 shows a typical activity profile for a Ni-YSZ sample for methane steam reforming. The material was first reduced at 700°C for 1 hour, followed by reaction at 700°C with a feed comprising $H_2O/CH_4/H_2 = 3/1/1$. A decrease in activity by approximately 80% can be observed relative to the fresh catalyst activity. We have consistently seen this type of result over many runs. TEM measurements were carried out on both the fresh (following reduction) and spent (after 65 hours on-stream) samples obtained from the run displayed in Figure 1. The TEM photos are shown in Figures 2 and 3. What we observe with the freshly reduced sample is a large quantity of small Ni crystallites on the surface of the YSZ. The size is typically in the range of 5-20 nm. Following reaction, some crystallites remain, but they have increased in size to typically 20-50 nm. We do not see evidence of carbon on this sample. The change

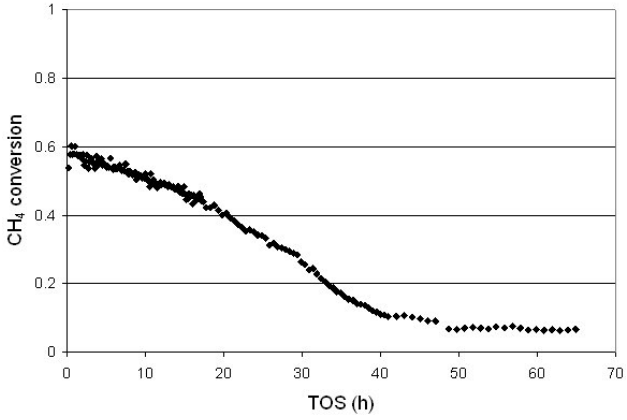

FIGURE 1. Deactivation of Ni-YSZ during Methane Steam Reforming at 700°C, GHSV = 200K, $H_2O/CH_4/H_2$ = 3/1/1

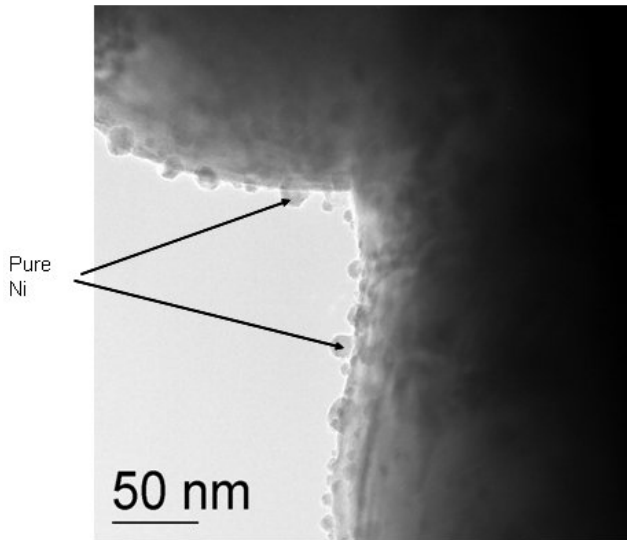

FIGURE 2. TEM of Ni-YSZ after 1 Hour Reduction at 700°C Showing Appearance of Small Ni Crystallites Attached to the Surface of the YSZ Particle

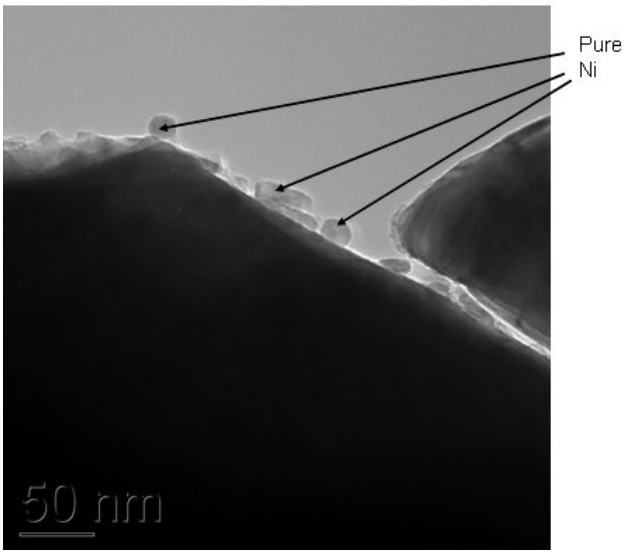

FIGURE 3. TEM of Ni-YSZ after 65 Hours SMR at 700°C, S/C=3, Showing Significant Nickel Particle Sintering

in crystallite size of the Ni particles is due to sintering, facilitated by steam in the presence of hydrogen [1]. The decrease in reforming activity with time is consistent with loss of surface area due to sintering of the Ni crystallites. The lined-out activity reflects that a steady state has been reached, and that further sintering is minimal on the time scale of the experiment. Clearly, if there were no small crystallites present, the activity could be significantly lower, and we have confirmed that by intentionally sintering the sample to the point where no small crystallites are observed. In that case, activity is decreased by at least an additional order of magnitude.

TGA Analysis and Carbon Deposition

We have found that deposition of carbon on Ni-YSZ during steam methane reforming (SMR) is not necessarily reflected in measured catalyst activity with time. Moreover, deactivation due to Ni sintering provides an additional complication, in terms of activity profile, that precludes directly correlating carbon deposition with a decline in activity. Although post-analysis of spent samples by microscopy (TEM) is an effective method to qualitatively measure carbon, this method is not quantitative and does not provide information regarding the rate of carbon formation as a function of conditions. We have implemented TGA analysis to provide a better direct measurement of carbon deposition as the reaction proceeds. Table 1 summarizes the results of TGA measurements of Ni-YSZ exposed to methane steam reforming at three different S/C ratios: 3/1, 2/1, and 1/1. The table also includes results for a Ni-MgO-YSZ sample at 1/1 S/C ratio. MgO- modified Ni-YSZ anode material was synthesized by the glycine nitrate process. In this case, diluted feeds were utilized because of specific laboratory safety precautions and regulations. The results demonstrate a clear effect of S/C ratio on carbon deposition, and it appears that a value of 3 is necessary to maintain carbon to very low levels. On the other hand, very low carbon is deposited with the Ni-MgO-YSZ anode material even at S/C = 1, demonstrating the increased tolerance generated by addition of the MgO. This is consistent with previously reported results by Singh et. al. [2].

TABLE 1. Effect of S/C Ratio on Carbon Deposition with Ni-YSZ and Ni-MgO-YSZ at 700°C

Catalyst	S/C ratio	Weight gain after 20 hours in SR conditions
Ni-YSZ (40% Ni), calcined at 1,375°C	1	~10.6%
Ni-YSZ (40% Ni), calcined at 1,375°C	2	~3.0
Ni-YSZ (40% Ni), calcined at 1,375°C	3	0.2-0.3%
Ni-MgO-YSZ prepared by glycine nitrate, calcined at 800°C	1	0.9
Ni-MgO-YSZ prepared by glycine nitrate, calcined at 1,400°C	1	1.0

Testing of Ni-YSZ Anode Plates

The actual operation of the fuel cell under on-anode reforming conditions will be substantially different from conditions of our Ni-YSZ powder tests. In addition to flow-by rather than flow-through conditions, the porosity of the formed anode will generate diffusion resistances so that the full thickness of the anode might not be utilized. In addition, it is known that the rate of electrochemical oxidation of H_2 and CO is significantly lower than the rate of methane steam reforming with nickel, hence the concern regarding the possibility of generating large endotherms at the front edge of the cell. To move toward more practical operation of the Ni-YSZ anodes for on-cell reforming, we have constructed a reactor that allows testing of the bulk anode for methane steam reforming and allows obtaining thermal profiles both along the flow path and across the anode. The reactor will allow accommodation of different plate thicknesses and lengths in order to determine the depth of penetration of the reacting gases and to determine the extent of reaction along the length of the anode plate. A photograph of the reactor is provided in Figure 4.

FIGURE 4. Ni anode plate reactor designed to operate under realistic flow conditions and to monitor temperatures at several points on the Ni-YSZ plate during reaction. Holes on sides are for cartridge heaters. Tubing extending from the reactor provides access of thermocouples to surface of plate at various locations.

Conclusions and Future Directions

Ni-YSZ under powder testing with flow-through operation shows initial activity decline followed by leveling of activity after tens of hours of operation. As confirmed by TEM results, deactivation is caused by the sintering during reaction of small nickel particles that are sitting on the surface of YSZ particles. These particles likely initially form as nickel evolves from the YSZ matrix (present as NiO) during reduction pretreatment. By controlling this sintering behavior, it appears possible to control the anode activity toward methane steam reforming.

TGA analysis has shown to be effective in measuring the extent of carbon formation during steam reforming reactions over Ni-YSZ. Preliminary results indicate that S/C ratios of 3 may be required to maintain carbon deposition at a low level.

Future directions include:

- Quantify effect of time/temperature/steam concentration on sintering of Ni particles present in reduced Ni-YSZ samples.
- Determine if intentional sintering of Ni-YSZ under controlled conditions provides a viable approach to adjusting catalytic activity for proper thermal management of the cell.
- Obtain activity data, thermal profiles, and activity maintenance data with anode plates in new reactor and quantify amount of thermal gradients formed.
- Evaluate various methods to add Cu to Ni-YSZ to control catalyst activity, and demonstrate the best method using a formed anode in the thermal profile reactor test.
- Compare addition of MgO and CeO_2 to Ni-YSZ for resistance to carbon formation at low S/C ratios, and develop the best synthetic method to implement this material modification.

FY 2006 Publications/Presentations

1. D.L. King, Y. Wang, Y.H. Chin, H.S. Roh, "Development of Modified Nickel-Based Compositions For On-Anode Reforming", SECA Core Technology Program Peer Review presentation, Lakewood, Colorado, October 2005.

2. D.L. King, Y.H. Chin, Y. Wang, H.S. Roh, P. Singh, "Investigation of Supported Bimetallic Ni-Au Steam Reforming Catalysts: Structure and Reactivity", SECA Topical Report, May 2006.

References

1. J. Sehested, Catalysis Today, 111 (2006) 103-110.

2. P. Singh, R. J. Ruka and R.A. George, US Patent 4,894,297, 1990.